

asserts that both Czekai '331 and '705 disclose solid particles having size and composition similar to that of the present invention. Applicants respectfully traverse.

***Distinctions Between the Present Invention and Czekai '331 and Czekai '705***

Czekai '331 and Czekai '705 disclose media which are different from the media currently claimed. In particular, Czekai '331 and Czekai '705 fail to disclose or suggest a media having a bulk density of  $4.0 \text{ g/cm}^3$  or more. In contrast, the present claims require that the bulk density of the media be  $4.0 \text{ g/cm}^3$  or more.

In Czekai '331, polymeric resins are employed as media and Czekai '331 describes that the density of the polymeric resins can be  $0.9$  to  $3.0 \text{ g/cm}^3$ . In this regard, please refer to column 2, lines 58-61 of Czekai '331. This density value is much lower than that required by the present claims. Moreover, in the working examples of Czekai '331, a polystyrene is used as a polymeric resin milling media. The densities of amorphous and crystalline polystyrenes are  $1.04$ - $1.065 \text{ g/cm}^3$  and  $1.12 \text{ g/cm}^3$ , respectively. These densities are much lower than the bulk density required by the present claims. Czekai '705 also employs a media in the working examples which uses polystyrene. As support for the densities of amorphous and crystalline polystyrenes, Applicants are enclosing herewith an excerpt from

"Concise Encyclopedia of Chemical Technology" (cover sheet, inside page and page 1115).

Applicants further point out that the Vickers hardness of polystyrene is about 20 MPa at the most. This value is about one five hundredth of the Vickers hardness value for the present invention. In particular, Applicants note that the present claims require the Vickers hardness to be 10 GPa or more. In this regard, Applicants enclose herewith Figure 1 of "Effect of  $\gamma$ -Irradiation on Hardness of Polymers", *Indian Journal of Pure Applied Physics*, Volume 23, February 1985, pages 103-104, as evidence of the Vickers hardness of polystyrene.

Applicants further submit that when such polystyrene media is used in preparation of a dispersion, the dispersion efficiency is completely unsatisfactory compared to the method of the present invention. Further, a method using such media is inferior in productivity due to the fact that it requires batch treatment to filtrate and separate the media from the dispersed solution. In contrast, according to the present invention, the media is separated from the dispersion while conducting dispersion.

In view of the failure of Czekai '331 and Czekai '705 to suggest or disclose the correctly claimed subject matter, Applicants submit that there exists no anticipation by either reference of the present invention. Moreover, no *prima facie* case of obviousness exists. Even if, *arguendo*, a *prima facie* case of

Application No.: 09/409,680  
obviousness has hypothetically been established, Applicants submit that unexpected results exist to rebut such a hypothetical case.

In order to further illustrate the unexpectedly advantageous properties of the present invention compared to Czekai '331 and Czekai '705, Applicants have prepared a Declaration. The Declaration presents comparative tests using the polystyrene media as disclosed in Czekai '331 and Czekai '705. In the Declaration, a solid fine-grain dispersion according to the present invention is compared with a solid fine-grain dispersion in which the media has been replaced with the polystyrene media as used in Sample 1, I-3 in Example 1 of Czekai '331. Moreover, a similar comparison is made between a solid fine-grain dispersion according to the present invention and a solid fine-grain dispersion wherein the media is replaced with the polystyrene media used in Sample S-3 in Example 1 of Czekai '705. The conditions and properties of the inventive solid fine-grain dispersions and the comparative solid-grain dispersions according to Czekai '331 and Czekai '705 are illustrated in Table A of the Declaration.

A review of the results in Table A reveals that the dispersion according to the present invention was obtained in a much shorter time period with a much smaller grain size compared with the dispersions of Czekai '331 and Czekai '705. Moreover, the average grain size according to the present invention was

much smaller than that according to Czekai '331 and Czekai '705. In view of these unexpected results, it is apparent that use of the media according to the present invention, having a specific size and hardness, allows for the creation of a fine dispersion with great efficiency as compared to Czekai '331 and Czekai '705. Accordingly, the presently claimed subject matter is unexpectedly superior over the primary references of Czekai '331 and Czekai '705.

It was shown above that Czekai '705 and Czekai '331 fail to disclose or suggest the specifically claimed bulk density or Vickers hardness of the present invention. Accordingly, the Examiner has failed to establish either anticipation or *prima facie* obviousness of the present claims. Even if, *arguendo*, the Examiner has hypothetically established a *prima facie* case of obviousness, Applicants respectfully submit that the unexpected results attached hereto rebut any hypothetical *prima facie* case of obviousness. Accordingly, the Examiner is respectfully requested to withdraw these rejections.

***Issues Under 35 U.S.C. § 103(a)***

The Examiner has rejected claims 13-16, 22, 23, 29 and 30 under 35 U.S.C. § 103(a) as being obvious over Czekai '331 and Czekai '705 in view of Lobo et al., USP 5,589,322 (hereinafter referred to as Lobo '322). The Examiner has also rejected claims 12, 21 and 28 under 35 U.S.C. § 103(a) as being obvious over

Czekai '331 and Czekai '705 in view of Scaringe et al., USP 5,750,323 (hereinafter referred to as Scaringe '323). Lastly, the Examiner has rejected claims 1-6 under 35 U.S.C. § 103(a) as being obvious over Czekai '705 combined with Canepa et al., USP 4,620,673 (hereinafter referred to as Canepa '673), Bishop, USP 5,474,237 (hereinafter referred to as Bishop '237) or Inkyo et al., USP 5,882,246 (hereinafter referred to as Inkyo '246).

Applicants respectfully traverse each of the above rejections.

Applicants respectfully submit that none of the secondary references relied on by the Examiner are able to cure the deficiencies of the primary references. That is, none of the secondary references discloses the currently claimed combination of elements including the specific density and Vickers hardness. Accordingly, the Examiner has failed to present a *prima facie* case of obviousness. Moreover, as indicated above, the unexpected results according to the present invention compared to the primary references of Czekai '331 and Czekai '705 rebut any hypothetical *prima facie* case of obviousness. Accordingly, the Examiner is respectfully requested to withdraw all of the above rejections.

In view of the above, Applicants respectfully submit that the present claims define subject matter which is patentable over the prior art of record. In particular, Applicants respectfully submit that the present claims define subject matter which is

Application No.: 09/409,680

patentable over the Czekai '331, Czekai '705, Lobo '332, Scaringe '323, Canepa '673, Bishop '237 and Inkyo '246 references. Accordingly, the Examiner is respectfully requested to withdraw all rejections and allow the currently pending claims.

If the Examiner has any questions or comments, please contact Craig A. McRobbie, Reg. No. 42,874, Reg. No. 42,874, at the Offices of Birch, Stewart, Kolasch & Birch, LLP.

Pursuant to the provisions of 37 C.F.R. §§ 1.17 and 1.136(a), the Applicants hereby petition for an extension of three (3) months to December 21, 2000 in which to file a reply to the Office Action. The required fee of \$890.00 is enclosed herewith.


If necessary, the Commissioner is hereby authorized in this, concurrent, and future replies, to charge payment or credit any overpayment to Deposit Account No. 02-2448 for any additional fees required under 37 C.F.R. § 1.16 or under 37 C.F.R. § 1.17; particularly, extension of time fees.

Respectfully submitted,

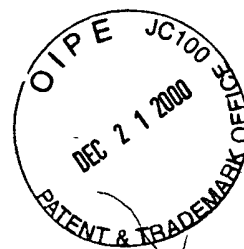
BIRCH, STEWART, KOLASCH & BIRCH, LLP

By: 

Marc S. Weiner  
Reg. No. 32,181  
P. O. Box 747  
Falls Church, VA 22040-0747  
(703) 205-8000

  
MSW/CAM/bsh  
enclosure:

Declaration of Masatoshi NAKANISHI  
Excerpt from Concise Encyclopedia of Chemical  
Technology  
Excerpt from Effect of  $\gamma$ -Irradiation on Hardness of  
Polymers



**KIRK-OTHMER**

# **CONCISE ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY**

RECEIVED  
DEC 23 2000  
TC 1700 MAIL ROOM

A WILEY-INTERSCIENCE PUBLICATION

**John Wiley & Sons**

NEW YORK • CHICHESTER • BRISBANE • TORONTO • SINGAPORE

Copyright © 1985 by John Wiley & Sons, Inc.

All rights reserved. Published simultaneously in Canada.

Reproduction or translation of any part of this work beyond that permitted by Section 107 or 108 of the 1976 United States Copyright Act without the permission of the copyright owner is unlawful. Requests for permission or further information should be addressed to the Permissions Department, John Wiley & Sons, Inc.

**Library of Congress Cataloging in Publication Data:**

Main entry under title:

Kirk-Othmer Concise encyclopedia of chemical technology.

"A Wiley-Interscience publication."

Abridged version of the 24 volume Encyclopedia of chemical technology. 3rd ed. New York: Wiley, c1978-c1984.

Includes index.

Executive editor, Martin Grayson; associate editor, David Eckroth.

I. Chemistry, Technical—Dictionaries. I. Kirk, Raymond E. (Raymond Eller), 1890–1957. II. Othmer, Donald F. (Donald Frederick), 1904–. III. Grayson, Martin. IV. Eckroth, David. V. Encyclopedia of chemical technology. VI. Title: Concise encyclopedia of chemical technology.

TP9.K54 1985 660'.03'21 84-22006  
ISBN 0-471-86977-5

Printed in the United States of America

10 9 8 7 6 5 4 3 2



K.R. Coulter, H. Kehde, and B.F. Hiscock, in E.C. Leonard, ed., *Vinyl Monomers*, Interscience Publishers, a division of John Wiley & Sons, Inc., New York, 1969.

**STYRENE-BUTADIENE SOLUTION COPOLYMERS.** See Elastomers, synthetic.

## STYRENE PLASTICS

Polystyrene (PS), the parent of the styrene plastics, is a high molecular weight linear polymer,  $[\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2]_n$ . The commercially useful form is amorphous and highly transparent. Under ambient conditions, the polymer is stiff and clear, whereas above the glass-transition temperature it becomes a viscous liquid which can be easily fabricated. Monomeric styrene is a worldwide commodity chemical. Polystyrene, a product family with as many as 30 members, although not a commodity in the same sense, is produced on a very large scale. Butadiene-based rubbers increase impact resistance, and copolymerization of styrene with acrylonitrile produces heat-resistant and solvent-resistant plastics. Packaging applications are the largest use for styrene plastics (see Acrylonitrile polymers).

### Properties

Considerable differences in performance can be achieved by using the various styrene plastics. For molecular weights above 5000, many properties are independent of chain length. The densities of amorphous and crystalline PS are 1.04–1.065 and 1.12 g/cm<sup>3</sup>, respectively;  $T_m = 240$ –250; refractive index,  $n_D = 1.60$ ; and the compressive modulus = 3000 MPa (435,000 psi).

The strain energy, derived from the area under the stress-strain curve shown in Figure 1, indicates the toughness of a polymer. High impact polystyrene (HIPS) has a higher strain energy than ABS plastics, although the latter are usually tougher. Tensile strengths of styrene polymers vary with temperature. Increased temperature lowers the strength.

The molecular orientation of the polymer in a fabricated specimen can significantly alter the stress-strain data, as compared with an isotropic specimen. For example, tensile strengths as high as 120 MPa (18,000 psi) have been reported for PS films and fibers. Polystyrene tensile strengths below 14 MPa (2000 psi) have been obtained in the direction perpendicular to the flow.

Creep tests involve the measurement of deformation as a function of time at constant stress. At room temperature, styrene and its copolymers show low elongation with only small variation with stress.

Stress-relaxation measurements, where stress decay is measured as a function of time at constant strain, have also been used to predict the long-term behavior of styrene-based plastics.

Fatigue is of considerable interest, and the inherent fatigue resistance of the material is tested and the relationship between specimen design and fatigue failure is determined.

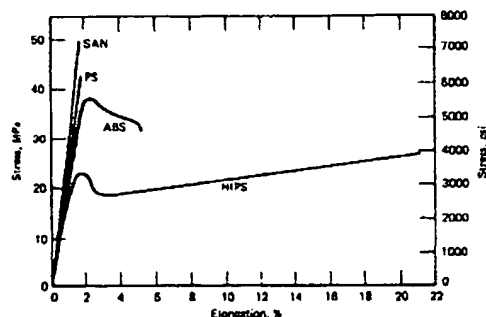


Figure 1. Stress-strain curves for styrene-based plastics.

Polystyrene and styrene copolymers are brittle. Rubber-modified styrene polymers are more impact resistant. A brittle fracture of a styrene polymer can be brought about by producing uniaxially oriented moldings. Tough moldings can be obtained through the introduction of balanced, multiaxial orientation. Embrittlement of tough rubber-modified styrene polymers occurs through aging.

Polystyrene and copolymers. Polystyrene,  $\bar{M}_w = 2-3 \times 10^5$ , is a crystal-clear, hard, rigid thermoplastic free of odor and taste. In addition, PS materials have excellent thermal and electrical properties. When lubricants are added, easy-flow materials are produced.

Standard polystyrenes are carefully prepared and characterized materials available from the National Bureau of Standards and the Pressure Chemical Company. Monodisperse polystyrene latices are produced by Dow Chemical as calibration for scientific measurements.

Isotactic polystyrene can be obtained by polymerization with stereospecific catalysts of the Ziegler-Natta type. It can be crystallized and has a threefold helix-chain conformation.

Crystalline polystyrene has a high melting temperature indicating a first-order transition temperature of ca 240°C. It is insoluble in most polystyrene solvents. The density of the 100% crystalline polymer is calculated to be 1.12 g/cm<sup>3</sup> from x-ray data. Although highly isotactic polystyrene has been prepared, only partially crystalline polymers have been obtained and generally with less than 50% relative crystallinity. The lack of commercial interest in isotactic polystyrene may result in part from its low degree of crystallinity and its slow crystallization rate. Syndiotactic polystyrene is unknown.

Polymers containing flame retardants (qv) have been developed. The addition of flame retardants does not make a polymer noncombustible, but increases its resistance to ignition and reduces the rate of burning with minor fire sources.

Antistatic polystyrenes have been developed. For styrene-based polymers, alkyl and/or aryl amines, amides, quaternary ammonium compounds (qv), anionics, etc. are used.

Acrylonitrile, butadiene,  $\alpha$ -methylstyrene, methyl methacrylate, and maleic anhydride have been copolymerized with styrene to yield commercially significant copolymers.

Butadiene copolymers are rubbers. Many latex paints are based on styrene-butadiene. Most block copolymers prepared in the presence of anionic catalysts, eg, butyllithium, are elastomers; some are thermoplastic rubbers.

Methyl methacrylate copolymers with styrene are clear materials which, when properly stabilized, are similar in their light stability to poly(methyl methacrylate). Maleic anhydride copolymers with styrene tend to have alternating structures. Accordingly, equimolar copolymers are normally produced, corresponding to 48 wt% maleic anhydride.

Some polymers from styrene derivatives meet specific market demands. For example, monomeric chlorostyrene is useful in glass-reinforced polyester recipes.

Rubber is incorporated into polystyrene to impart toughness. The resulting materials are called high impact polystyrenes (HIPS). The rubber is dispersed in the polystyrene matrix in the form of discrete particles.

Acrylonitrile-butadiene-styrene (ABS) polymers are also two-phase systems in which the elastomer component is dispersed in the rigid styrene-acrylonitrile (SAN) copolymer matrix. They are rigid at room temperature, and have excellent notched impact strength. This combination makes ABS polymers suitable for demanding applications. Several ABS polymers exhibit a minimum tendency to orient or develop mechanical anisotropy during molding. Accordingly, uniform tough moldings are obtained. In addition, ABS polymers exhibit good ease of fabrication and produce moldings and extrusions with excellent gloss, which can be decorated by many techniques. Some of the high rubber compositions are excellent impact modifiers for poly(vinyl chloride) (PVC).

Glass-reinforced styrene polymers. Glass reinforcement of PS and SAN markedly improves their mechanical properties; strength, stiffness, and fracture toughness are generally at least doubled. Creep and relaxation rates are significantly reduced and creep rupture times are increased. The coefficient of thermal expansion is reduced by more than one half, and response to temperature changes is minimized. Glass-rein-

Indian Journal of Pure & Applied Physics  
Vol. 23, February 1985, pp. 103-104



## Effect of $\gamma$ -Irradiation on Hardness of Polymers

M H ANSARI, R PANDEY, P PARASHAR & S C DATI  
Department of Postgraduate Studies & Research in Physics, Rani  
Durgavati Vishwavidyalaya, Jabalpur 482 001

Received 3 May 1983; revised received 13 May 1984

Polystyrene and polypropylene specimens were irradiated with  $\gamma$ -irradiation doses ranging from 1-15 Mrad. Vickers hardness number ( $H_v$ ) has been calculated for pure and irradiated specimens. It has been found that  $H_v$  increases with radiation dose up to 10 Mrad and becomes almost constant. The increase in  $H_v$  for polystyrene is about 25% whereas it is only 12.5% for polypropylene. However,  $H_v$  also decreases up to 3 Mrad in the case of polypropylene. The variation of  $H_v$  with  $\gamma$ -irradiation has been explained on the basis of crosslinking and crystallinity of polymers.

The scope of application of polymers has increased considerably due to a rapid progress in the nuclear and space sciences and technology. Polymers are, therefore, required to act satisfactorily under various levels of high energy radiation. It is well known that the mechanical properties of polymers undergo both transient and permanent changes in a radiation field<sup>1-6</sup>. Amongst the mechanical properties, although a great deal of work has been reported on the variation of tensile strength with radiation, not much detailed information is available with regard to the radiation effect on the hardness of polymers. Therefore, it is worthwhile to carry out a study of hardness of  $\gamma$ -irradiated polymeric samples. This note reports the effect of  $\gamma$ -irradiation on hardness of polystyrene and polypropylene.

Sample of polystyrene (styron 685) used for the present study was obtained from M/s Dow Chemical Co. USA. The polymer was dissolved in purified benzene and the solution was filtered. Films of polystyrene (PS) of about 0.5 mm thickness were obtained by pouring the solution on a cleaned optically plane glass plate floating on mercury. After the solvent evaporated, the film was gently lifted off the glass plate. The films were then annealed in air at 70°C for 8 hr and were subjected to room temperature outgassing at  $10^{-4}$  Torr for 24 hr. For polypropylene (PP), commercially available films of about 0.5 mm thickness were used. The specimens were irradiated with  $\gamma$ -radiation of doses ranging from 1-15 Mrad by using cobalt-60 irradiator at the Bhabha Atomic Research Centre (BARC) Bombay. The indentations were carried out by mhp 160 microhardness tester with a Vickers diamond pyramidal indenter with square base

and 136° pyramid angle, attached to Carl-Zeiss NU2 universal research microscope. The load was varied from 5 to 150 g. The diameters of the indentations were measured using a micrometer eyepiece. The Vickers hardness number ( $H_v$ ) was calculated from the relation:

$$H_v = 1.854L/d^2 \text{ (kg/mm}^2\text{)}$$

where  $L$  is load in kg and  $d$  the diameter of indentation in mm. For each test, the duration of the indentation was kept 30 s. For the same load, at least 10 indentations were made at different points of the sample and average hardness number was computed. During the indentation the samples were kept strictly horizontal and rigid.

Fig. 1 shows the variation of Vickers hardness number with load for pure and irradiated specimens. It is evident that the variation of  $H_v$  is more for small stresses and then it becomes almost constant after 50 g. For small stresses, the deformation may be elastic and the material recovers on removal of the stress resulting in a rapid change in  $H_v$ .

Figs 2 and 3 show the variation of  $H_v$  with radiation doses at a constant load of 50 g for PP and PS, respectively. It is evident that for a constant load,  $H_v$  increases with radiation up to a dose of 10 Mrad and then becomes constant. Interaction between the polymer and the field results in the deposition of energy within the specimen. This may produce extensive physico-chemical changes in crosslinking, molecular weight, and crystallinity, etc. Due to this, the physical properties may also exhibit changes. Crosslinking of

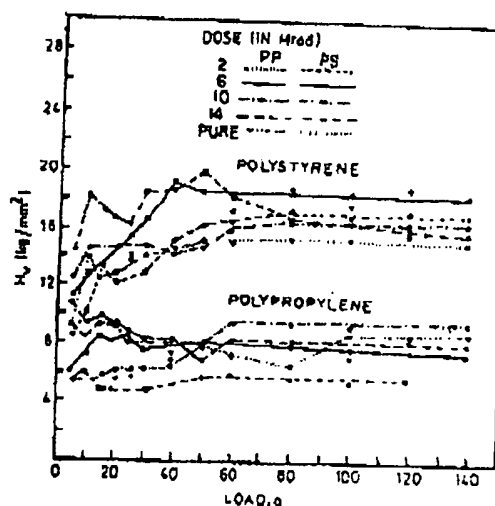
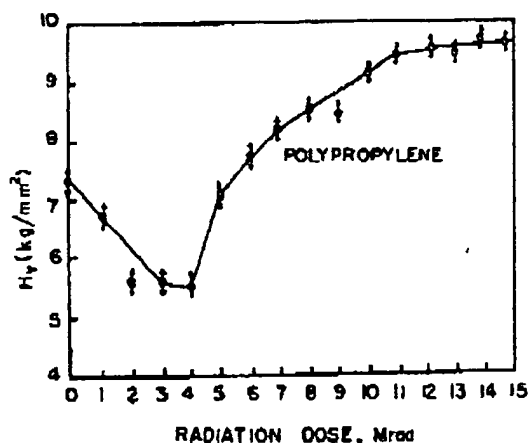


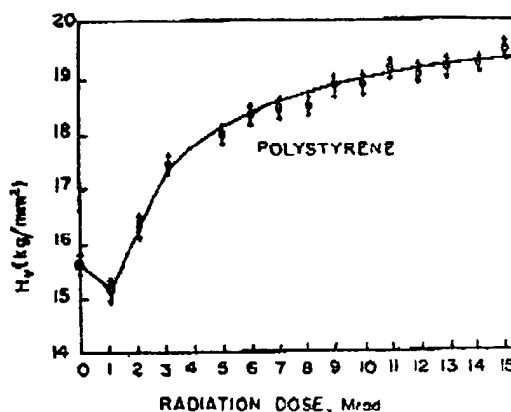
Fig. 1—Variation of  $H_v$  with load

## INDIAN J PURE &amp; APPL PHYS, VOL 23, FEBRUARY 1985

Fig. 2—Variation of  $H_v$  with  $\gamma$ -irradiation for polypropylene

polymer under the action of ionizing radiation is known as radiation crosslinking<sup>7</sup>. Increase in crosslinking density restricts the mobility of the molecular chain. With the increase in the dose of irradiation, the crosslink density also increases but it becomes constant at a certain dose, after which molecular chains become rigid and  $H_v$  becomes almost constant. In the present case, this is found to occur at the radiation dose of 10 Mrad.

It is evident from Fig. 2 that for PP, there is a decrease in hardness number up to a dose of 3 Mrad, whereas the hardness number increases continuously for higher doses and is about 12.5% for a dose of 10 Mrad. Also, after this dose the specimen becomes brittle. The decrease in hardness constant may be explained by assuming that scission of molecules of PP is greater than crosslinking, for small doses of radiation. The scission of molecular chains reduces the average molecular weight of the polymers and thus the binding forces such as intermolecular forces, van der Waals forces, etc. get reduced. As a result of this, on

Fig. 3—Variation of  $H_v$  with  $\gamma$ -irradiation for polystyrene

indentation with the same load, the slipping of the molecular chains increases and the deformation produced also increases. Consequently, the hardness number,  $H_v$  of the polymer decreases. In the case of PS (Fig. 3), the hardness number increases with irradiation dose by about 25%. Thus in the case of PP and PS, the hardness increases with radiation dose. However, there is a decrease in hardness for small doses.

The authors are grateful to the Chemistry Division, BARC, Bombay, for providing  $\gamma$ -irradiation facilities. Two of the authors (RP and PP) are thankful to the University Grants Commission, New Delhi, for the award of junior research fellowships.

## References

- 1 Harris J S & Dard I M, *J Mater Sci (GB)*, 5 (1970) 571.
- 2 Andrews E H, *Macromol Sci (USA)*, 8 (1972) 227.
- 3 Grubb D T, Kellar A & Groves G M, *J Polym Sci Part II (USA)*, (1972) 753.
- 4 Dlugosz J & Kellar A, *J Appl Phys (USA)*, 39 (1968) 5775.
- 5 Charlesby A, *Atomic radiation & polymers* (Pergamon Press, Oxford) 1960.
- 6 Lawton E J, Bueche A M & Balwit J S, *Nature (GB)*, 172 (1953) 76.
- 7 Tsegar A, *Physical chemistry of polymers* (Mir Publishers, Moscow) 1972, 68, 94.